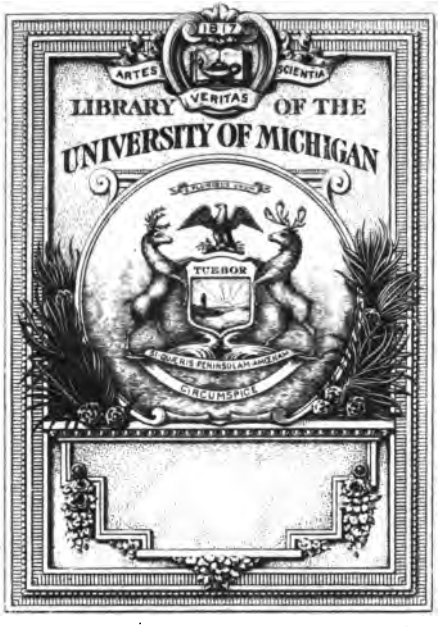

A Contribution to the Investigation of the Temperature Coefficient of Osmotic Pressure; a Redetermination of the Osmotic Pressures of Cane Sugar Solutions at 20°

DISSERTATION

SUBMITTED TO THE

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CONTENTS.

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This investigation was carried out under the supervision of Professor Morse, to whom the author wishes to express his gratitude for instruction in lecture room and laboratory. The measurements of osmotic pressures were made in collaboration with Dr. Zeis, Dr. Holland, Mr. Carpenter and Mr. Meyers, and special credit is due Dr. Zeis, who was in charge of the measurements from Oct. 1 to March 1.

I desire to thank Dr. Turner and Dr. Pfund for helpful suggestions, and to express my obligation to President Remsen, Professor Jones, Professor Acree, Professor Bliss and Dr. Pfund for instruction.

PREFACE.

The investigation here recorded was a study of the osmotic pressures of cane sugar solutions at 20°. It is one of a series of investigations having for their object the establishment of the temperature coefficient of the osmotic pressures of cane sugar solutions, ranging in concentration from one-tenth *weight*[1] normal, to normal at intervals of 5° between 0° and 25°-30°.

Those phases of the subject which are dealt with in this paper are:

1. Purification and analysis of the cane sugar.
2. Improvements in apparatus.
3. The measurements at 20° and their discussion.

1 Morse, Frazer and Dunbar, Am. Chem. J., 38, 2, '07.

PURIFICATION AND ANALYSIS OF THE CANE SUGAR.

The methods in use at this laboratory for measuring osmotic pressures having reached a high state of accuracy it became desirable to make the measurements with a single stock of sugar of known purity. Previously, while the methods were in a less satisfactory state, the sugar used was the purest obtainable commercial rock candy, the uniformity of which was only assured within certain limits.

The method of purification employed was essentially that described by Cohen and Commelin[1]. The original material was a rock candy crystalized by a local firm. This was ground in a porcelain mortar, and dissolved in previously boiled, distilled water, warmed in a porcelain dish over a water bath for not longer than twenty minutes, and at a temperature never allowed to exceed 60°. When approximate saturation was obtained in this manner, the solution was quickly filtered with suction, and precipitated with 98% ethyl alcohol, which had previously been distilled from lime through a column of beads. Samples of this alcohol were tested from time to time and found free of lime. The precipitated sugar was filtered with suction, and, after draining three to six hours, was washed with 85% ethyl alcohol. To make the washing the more thorough, the sugar was each time removed from the funnel, and stirred vigorously with the alcohol. Thirty-two kilo lots of the sugar at this stage were very carefully mixed, and then in small lots again subjected to the same process of purification. In addition to the washing with ethyl, hot methyl alcohol was used for the final washing. The separate precipitates were then thoroughly mixed with each other, dried at 60°, and bottled after another thorough mixing. Sixteen kilograms of this twice precipitated sugar constitutes the supply which has been drawn upon for all measurements since March 26th, 1909. Previously, since January 1st, a smaller sample of three times precipitated sugar had been used. A large portion of the stock has been kept over calcium chlorid to insure desiccation and the removal of alcohol before use.

In the following analyses "Sample A" designates the original rock candy, B the once precipitated, C the twice precipitated, and D a small preliminary batch which was carried through three precipitations.

1 Zt. Phys. Chem., 64, 1.

Combustion With Electric Furnace.

SAMPLE A.		SAMPLE B.		
%H.	%C.	%H.	%C.	
6.432	42.156	6.430	42.116	
(6.506	42.335)[1]	6.451	42.059	
6.495	42.081	6.465	42.151	
6.477	42.090			
6.488	42.109	6.445	42.108	Average
6.482	42.083	6.482	42.083	Theoretical
+.006	+.026	—.037	+.025	Difference

SAMPLE C.		SAMPLE D.		
%H.	%C.	%H.	%C.	
		6.484	42.047	
		6.410	42.104	
6.466	42.151	6.453	42.009	
6.420	42.081	6.487	42.031	
6.471	42.116	6.485	42.101	
6.452	42.116	6.464	42.058	Average
6.482	42.083	6.482	42.083	Theoretical
—.030	+.033	—.018	—.025	Difference

[1] Not averaged, although no error in the determination was detected.

Ash.

A large known weight of each sample was incinerated in a platinum crucible protected from the free flame by a porcelain dish. All samples showed an ash content of from 21 to 50 parts per million. Each residue gave a test for iron, although the sugar came into contact with iron at no time during the process of purification. In order to make sure that no contamination by the lime used in concentrating the alcohol had occurred, thirty-five grams of Sample C were charred, and partly incinerated to reduce its volume, and a spectroscopic examination for Ca was made with the electric arc and a Roland grating, and again with the Bunsen flame and a prism spectroscope. Duplicate examinations with different incinerated samples were made in each case. In no case was a trace of a calcium line discovered by visual or photographic exploration in the visual region of the spectra. Dr. Pfund, of the Department of Physics, who made the examination with the Roland grating, then photographed for the brilliant H and K lines of the ultra violet, and found them only in about the same intensity as in the photograph with the comparate blank carbons.

Reducing Sugars.

Analyses for reducing sugars were made in accordance with the directions described in *Methods of Analysis Adopted by the Association of Official Agricultural Chemists,*[1] "for materials containing 1% or less of invert sugar and a high percentage of sucrose." Since the precipitate in each case contained considerably less than 50 milligrams of copper, the lowest figure for copper in Hertzfeld's table, and since there is no statement either of the method of extrapolation or of the standard sugar used in preparing this table, the method was abandoned for that of Soldaini as modified by Ost.[2] Preliminary experiments with aliquot portions of known glucose solution gave,

1. 0.0089 g taken	2. 0.0089 g taken
0.0088 g found	0.0089 g found

Using 10 g. portions of each sample the following data were obtained. Ost's table for conversion of Cu to the equivalent of invert sugar formed the basis of the calculations:

Grams Cu. found.	Grams invert sugar calculated.	% of invert sugar in sample.	Sample
0.0277	0.0081		
0 0280	0.0082		
0.0293	0.0085		
0.0283	0.0083		
	0.0083	0.083%	A
0.0100	0.0017		
0.0137	0.0019		
0.0142	0.0018		
	0.0018	0.018%	B
0.0085	0.0017 less than		
0.0108	0.0018		
0.0106	0.0017		
0.0062	0.0017 less than		
less than	0.0017	less than 0.017%	C
0.0065	0.0017 less than		
less than	0.0017	less then 0.017%	D[1]

[1] Only one analysis of D made because of low supply.

According to these analyses, a normal solution of Sample C would be about $\frac{n}{3300}$ with respect to invert sugar. If we assume that one molecule of invert sugar takes the place of one

1 Bulletin 46, U. S. Dept. Agriculture.
2 Wiley; Practice of Agricultural Chemistry, Vol. III.

molecule of sucrose, and that the second molecule of the two, which together approximate the weight of one molecule of sucrose, is the only one which would produce an error in the osmotic pressure, then we may say that a normal solution of Sample C would have a true normality of approximately $1+\frac{1}{6800}$. A further striking qualitative difference between the original and purified samples should be noted. The original, at the moment of incipient boiling with the Soldaini reagent, formed a heavy green cloud, while with the purified sugars the reagent kept its fresh color and the precipitate was only noticed when filtered.

The United States Bureau of Standards has been given samples of A, B, C, and D, upon which it is conducting tests. A formal report of these has not yet been received. It will include determinations of the invert sugar, and of the rotations, in both of which the Bureau is making every effort to attain the greatest accuracy at present possible. A preliminary report[1] on the tests for invert sugar has been received in which it is stated that:

Sample	A	contains	between	0.09%	& 0.08%
"	B	"	"	0.02	& 0.01%
"	C	"	"	0.02	& 0.01%
"	D	"	less than		0.01%

The relative difference between B and C is about 0.003% and between C and D is 0.005%. A comparison of these determinations with those made in this laboratory will show that the agreement is fairly close in the third decimal place.

I think it permissible to quote from the informal report, that Sample D as regards invert sugar compares very favorably with the best prepared at the United States Bureau of Standards.

Freezing Point Lowerings.

Dr. Turner, of this laboratory, who made some very careful determinations of the freezing point lowerings of normal solutions of each sample, has kindly allowed me to publish his final averages. The details of his work will be published later. The following molecular lowerings for the normal solutions employed are accurate $+0.°001$, with their absolute, but not relative values subject to a possible slight modification when the thermometer is still more carefully calibrated.

Sample	A	$-2°.037$
"	B	$-2°.041$
"	C	$-2°.041$
"	D	$-2°.048$

1 By R. F. Jackson.

A slight but distinct gain in the molecular lowerings is seen to have resulted. That this occurred in spite of the distinct lowering in the content of invert sugar is strange. That it could be due to alcohol in the sugar is improbable, because some very careful tests failed to reveal any indications that alcohol was present, and, furthermore, because desiccation *in vacuo* over calcium chlorid gave ample opportunity and time for the removal of alcohol before the freezing point determinations were made. One consideration to which great importance is not attached is this. Hot methyl alcohol was used for the final washing of each of the purified samples. According to its comparatively greater solubility in methyl alcohol, raffinose, a normal constituent of cane sugar, should therefore have been rapidly removed. The assumption that raffinose of higher molecular weight than saccharose was rapidly removed by the methyl alcohol is in harmony with the observed increase in molecular lowerings.

A summary of the analyses of Sample C, the stock used in the measurements of osmotic pressures, is now given.

% Carbon	42.166
% Hydrogen	6.452
% Invert Sugar	0 01–0.02
% Ash	about 0.003
Iron	trace
Calcium	none
Alcohol	none
Normal molecular lowering of freezing point	−2°.041

IMPROVEMENTS IN APPARATUS.

The apparatus and methods used at this laboratory in determining osmotic pressures, have been described in previous publications.[1] A few minor improvements are to be noted.

Those who have followed the work will recall that the principle of temperature regulation employed is to pump the water rapidly over coils of pipe kept by running water a little below the temperature desired in the bath, and then over an electric stove, which is controlled by a thermostat. By regulation of the thermostat any desired temperature may be maintained between that to which the cooling pipes can lower the water and that to which the electric stoves can warm it. The air space is kept at constant temperature in accordance with this same principle, a fan taking the place of the pump, and an electric light serving as stove. Because of the different heat

1 Morse & Frazer, Am. Chem. Jour., 28, 1 ('02).
Morse & Frazer, Am. Chem. Jour., 36, 1 ('06).
Morse & Lovelace, Ibid, 40, 4 ('08).
Morse & Mears, Ibid. 40, 3 ('08).
Morse & Holland, Ibid, 41, 2 ('09).

capacities of air and water and the different volumes of each in the bath, it was found advantageous to separate into two sections the cooling pipes which had previously been in series for the cooling of both air and water spaces. Each may now be separately controlled. Through the winter months the cooling pipes in the air space were not used because the temperature of the outside room was sufficiently low to produce the proper cooling. A more even temperature environment for the bath was furnished by the installation of a fan in the room outside the bath. Because of the relatively low heat capacity of air, the air space in the bath is the more difficult space to keep at constant temperature, but it can be done with a fair degree of success if the heating and cooling sources are nicely adjusted so that the air will not pass over either an excessively cool or an excessively warm surface.

For the maintenance of constant temperature we are of course dependent in large measure upon the sensitiveness of the mercury and glass thermostats. The least sparking of these will cause fouling of the mercury, and early in the year considerable trouble was definitely traced to this cause. The means which had been used to prevent this was the spanning of the spark gap by the proper resistance, either that of a 75 volt 16 candle power electric light filament, or that of graphite painted over a porcelain tube. To eliminate the sparking altogether, tin foil condensers are now used to span the spark gaps. Although these tin foil condensers alone give every evidence that they completely absorb the induced currents, which have caused sparking in the thermostats at the "break," we have "made assurance doubly sure" by leaving in parallel with each condenser as a "by pass" the resistance formerly used alone. Several thermostats which have been used in various baths about the laboratory, have worked perfectly since their spark gaps have been "spanned" with these condensers.

It has been noted that when the platinum point and the surface of the mercury are very clean the mercury will wet the platinum. The result is that, when the thermostat cools, the mercury still clings to the platinum point, and the breaking of the circuit will therefore occur at a slightly lower temperature than the "make." This is easily remedied by rubbing the finger over the platinum tip until it is found that the platinum will touch and leave the mercury meniscus sharply.

After these two sources of trouble were remedied the water space kept at 20° for a period of two months at a stretch to within about $\pm$ 0°.005 except at three observations, when the deviation was $+$0°.01, due to stoppage of the water in the cooling pipes. The air space during this period though far

more difficult to keep constant, did so with only an occasional observed deviation of $\pm$ 0°.05, except, of course, when the bath was opened to change the cells.

In order to insure constant temperature of the nitrogen volume of the manometers, it seemed desirable to eliminate as far as possible the heating effects of the electric light used in the readings. Accordingly, a device was made by which the infra red waves of the light were cut off. A 4% solution of nickel sulfate was used at the suggestion of Dr. Pfund, of the Department of Physics, and this was enclosed between glass plates, forming a screen about one inch thick. An eight candle power electric light bulb, frosted to provide a soft, diffused light, was placed behind this, and the intensity of the illumination increased by a reflector made of a silvered watch glass. Tests made with a thermocouple showed that the radiant energy emitted through the nickel sulfate screen was but 1% of that given by the unscreened light. The green color obtained by this method of illumination is also thought to enhance the detail of both mercury meniscus and silvered meter bar. One of these devices has been used in the determination of the normal volumes of the manometers.

THE MEASUREMENTS—PRELIMINARY DISCUSSION.

Since this investigation had for its object the establishment of one link in the chain of data whereby the temperature coefficient of osmotic pressures may be established, relative rather than absolute pressures were sought. With this in view the technique and conditions employed in measurements at other temperatures were followed as closely as possible.

In this connection attention should be called to two well recognized errors, which have but little significance in the present investigation, but which render the data somewhat inaccurate for the comparison of high with low pressures. In our manometer data the volume correction in calibration units for the double meniscus is taken as two-thirds the radius of the bore. This is based on the assumption that the meniscus in these small bores, of about half a millimeter diameter, is approximately hemispherical. Since it is known that the meniscus leaves the glass even in capillaries of this size at an angle much greater than zero, and since actual observation of the form of the meniscus shows it to be considerably less than hemispherical, the $2/3r$ correction is doubtless too large. With low pressures the error will be insignificant, but when the nitrogen is compressed to one twenty-seventh its volume

under standard conditions by the pressure of a normal solution, a small error in this small observed volume will produce a considerable error in the calculated pressure. It would, therefore, be unjust to claim for the present series of investigations great accuracy in the comparison of high with low pressures for the purpose of substantiating a law similar to Boyle's. But, since the normal volumes of the manometers are of about the same order of magnitude, and, since they are compressed to about equal degrees for the same concentration of sugar at the various temperatures employed, the error is of little significance in the purpose of the present series of measurements.

The second error, to which attention was called in 1907,[1] is one which, if it exists, makes the data inaccurate for the comparison of high with low pressures. But this again would not alter the value of the data for use in determining the temperature coefficient except perhaps by an indirect effect to which attention will be called later. The error lies in the possibility that the membrane formers are not isosmotic. If, for example, the concentration of the potassium ferrocyanid on the interior is less than osmotically equivalent to the copper sulfate on the exterior of the membrane, a constant positive correction should be applied in order to obtain the true osmotic pressure of the cane sugar. Obviously this constant correction would be of greater significance to the low than to the high pressures. But an example will show that this error would have to be large to affect the sought for temperature coefficient. Let us take a measurement of a 0.5N solution that gave an observed osmotic pressure of 11.890 atmospheres at 0°, and one of the same concentration that gave a pressure of 12.750 atmospheres at 20°. The "theoretical gas pressure" of such a solution is 11.133 atmospheres at 0°, and 11.950 at 20°. The ratio of osmotic to gas pressure for the former was found to be 1.068 and for the latter 1.067. Assume now that the potassium ferrocyanid and copper sulfate, used to protect the membrane, differ in osmotic pressure by as much as —0.03 atmposphere. Unless the potassium ferrocyanid itself affects the osmotic pressure of the cane sugar, we are justified in adding this 0.03 atmosphere to obtain the pressure due to the sugar alone. We then obtain as the corrected pressures 11.920 at zero, and 12.780 at 20°, giving for the ratio at zero 1.071 and for the ratio at 20°, 1.070. Each ratio is considerably changed by this correction, but each by the same amount, so far as the third decimal place is concerned, and hence the temperature

1 Am. Chem. Jour., May, 1907.

coefficient is seen to have remained unaltered. In this calculation the assumption has been made that the temperature coefficient of dissociation for the two membrane formers are practically equal in the range of temperature used.

Sources of error which would render the measurements inaccurate for the determination of the temperature coefficients have not been overlooked. A change of temperature in the air space of 0°.1 will not affect the ratio seriously, and can always be allowed for in the calculation; but a similar fluctuation in temperature in the water space, that is in the neighborhood of the cell itself, cannot be allowed for in the calculation, because it involves the expansion or contraction of cell, solution, brass cone and collar, and the mercury in the bulbs of the manometer. It has, therefore, been our practice to plug the tops of the cans, into which the cells are set, with cotton, so that any change of temperature in the air space could only permeate slowly to the cell and the bulbs of the manometers. Of the two hundred and eighty observations which are included in the following tables, fourteen were made when the temperature of the water bath varied from 20° more than 0.° 01, and in but two was the variation greater than 0.° 03. The variations in each of these two cases was 0.° 3. The maximum probable errors in weighing the solutions, of inclination of the manometers to the meter bar, and of the barometric readings, could only affect the ratio in the fourth decimal place. A recent calibration of the meter bar used with the cathetometer, shows a periodic error of 0.02 mm. for alternate millimeter marks. This in conjunction with the unavoidable errors in reading, may have affected the ratios of the higher concentrations to a very slight extent. We have sought to reduce the errors of reading to a minimum, both by check readings by two or more observers, and by keeping ignorant of the figures found on the previous observation. The agreement has been very satisfactory. In checking the concentration of the solutions before and after the measurements, by means of the saccharimeter, the agreement of different observers, and even of the same observer, has not been so satisfactory. After an extended series of comparative readings we are of the conclusion that for a solution of average clearness, darkened as it always is by the potassium ferrocyanid, 0.1 point on the scale of our Schimidt and Haensch saccharimeter is the limit of our accuracy. When the difference in rotation between the solution as made up and the solution at the close of an experiment, both compared at the same time and temperature, was distinctly as great as 0.1, we made it a practice to discard the measurement. All differences less than this are recorded as

"no loss in rotation." 0.1 point error in the saccharimeter reading corresponds to 0.001 in the ratio for a normal solution, 0.002 in the ratio for a 0.5n, and as much as 0.008 in the ratio for a 0.1 normal solution; and only within these limits are the ratios certain to be unaffected by change in the concentration of the solutions.

We have, therefore, taken pains to prevent the dilution or concentration of the solution which inevitably accompanies four blunders in good technique. In the first place, the cells before being set up are filled and kept in thymol water. A thorough rinsing of the interior with the sugar solution is therefore necessary, else the solution will become diluted by the water which clings to the interior of the cell. Secondly, the solution which has been finally poured into the cell will, in exerting its osmotic pressure, cause water to permeate the membrane with resulting dilution of the solution, unless the manometer is quickly fastened in place and an initial "mechanical pressure" brought to bear by forcing the cone down into the cell so that the osmotic pressure of the solution is balanced by the gas pressure in the manometer. This one point caused considerable trouble in former years, when the means of securing the manometer in place was not developed. With the present arrangements, and "team" work, but few seconds elapse between the time when the solution is poured into the cell and the moment when, with the manometer firmly secured, the proper initial pressure is brought to bear by closing the exit tube and forcing the cone down by screwing up the brass collar. Rapid manipulation is also essential when the cell is taken down. In the third place, this initial pressure must be nicely adjusted to balance the probable osmotic pressure to be developed, since, if too small or too great an initial pressure is given, the solutions will be diluted or concentrated by a volume of water corresponding to the volume through which the mercury in the manometer must be forced in order to establish the equilibrium. The small bore of the manometer allows a little range in this, but in extreme cases, of which we have had some examples, concentration of the solution has been traced to the production of too great an initial pressure. Such cases have confirmed the statement,[1] "that the 'mechanical' pressure upon the solution must never exceed the maximum osmotic pressure." Concentration from this source may even escape detection because of the operation of one or more of the causes which subsequently produce dilution, and is consequently to be feared more than dilution. The fourth matter to which atten-

1 Am. Chem. Jour., Sept., 1908, p. 276.

tion should be paid, is the prevention of fluctuations in temperature just after the cell is set up. The cell in its bottle of 0.1n $CuSO_4$ is immediately placed in a small bath at the proper temperature, from which it may be conveniently removed from time to time for the adjustment of the initial pressure. But the manometer projects into the air above, which is, of course, at the temperature of the laboratory. The opening of a window, for instance, will alter the temperature of the nitrogen in the manometer, and it becomes troublesome to tell its pressure. We have been favored in working at 20° by the ease with which it is possible to keep the laboratory at nearly 20° during this preliminary manipulation.

An uncertainty occurs in the measurement of low pressures bv reason of the fact that the membrane is often slow in allowing the passage of sufficient water to compensate fluctuations in barometric pressure. The barometric pressure is, of course, subtracted from the sum of the pressures of nitrogen, capillary depression and liquids in the manometer to obtain the osmotic pressure. If the barometric pressure suddenly drops, and the membrane is slow in allowing the escape of sufficient water to compensate for this drop, the observed pressure of the solution is that of the osmotic pressure plus that of the former high barometer, and an error is made in subtracting the new low barometric pressure. This uncertainty is often evident when measuring the lower concentrations, but since the barometric pressure is small in relation to the osmotic pressure of high concentrations, barometric fluctuations have no noticeable effect upon these.

A very uncertain source of error lies in possible variations in the bore of the manometers, and the consequent variations in the capillary depression when the meniscus is at different points. This error also enters into the determination of the normal volume of a manometer. The capillary depression of each manometer is determined experimentally, but only for one point. From an inspection of the calibration curves of the manometers the bore is seen to vary in each case, but it is doubtful whether the variations are of sufficient magnitude to alter the capillary depression more than a few millimeters. This is a matter of some importance to determine experimentally, and it will be made the subject of an investigation when accuracy in other directions becomes sufficient to warrant it. In this connection attention might be called to a little point where care has been used in the present investigation. The lower part of the manometer is filled with solution around to the first bulb where it meets the mercury. If care is not taken to have the mercury in this bulb at the widest part when the

final pressure is developed, and the surface is actually near the upper constructed part, an appreciable capillary depression will obtain which is not allowed for in the calculations.

In accordance with the usage in the investigations at other temperatures, the capillary depression of each manometer has been reckoned as 0.02 atmosphere. As experimentally determined, they actually range from 0.015 to 0.023 atmosphere. Furthermore, the pressure of the solution measured from the surface of the liquid outside the membrane to its height at the point where it meets the mercury in the manometer, has in each case been taken as 0.01 atmosphere, altho it varies slightly with each manometer and with the density of the solution. By rounding off the values for both capillary depression and pressure of solution, no great error has been introduced, but the assumption should be noted.

It is to be regretted that more measurements which fulfill the requirements to be mentioned were not obtained. That they were not is believed to be due, in the main, to two causes. The cells available for the measurements had been used at 0°, 5° and 10°, and it has been observed, almost without exception, that cells used at a low temperature are of little avail for measurements at higher temperatures until after a long period of treatment. A reason for this will be mentioned in another connection. The cells used at 20° were, therefore, not in prime condition until January, and indeed there is some evidence that, in spite of the thymol, the slight growths of *Penicillium* which have been so troublesome in the past, may have infected parts of the cell wall. However that may be, by January manometer 6 had developed a flaw, and 5 was broken. As subsequent investigation has shown, we were left with only one reliable manometer, number 15, and possibly 21. Since the others were at the time supposed to be thoroughly reliable, they were often used to the exclusion of 15, and not until 15 was used continuously and 9 came upon the scene late in March, were reliable measurements obtained.

The criterions which the measurements have been required to fulfill in all the series, as well as in this, before they were adjudged acceptable were: 1. Constancy of temperature in air and water spaces. 2. Constancy of osmotic pressure for a period of at least twenty-four hours. 3. No change in the concentration of the solution that could be detected with the saccharimeter. 4. No fault which could be detected in the technique or in the apparatus.

Of the 163 experiments made at 20°, 127 had to be rejected as not fulfilling one or more of the above requirements. The remaining 36 are recorded in the following tables.

TABLE A.

Concentration.	No. of Experiment.	Date.	Cell.	Resistance.	Monometer.	Volume.	Average O. P.	Theoretical Gas Pressure.	Difference.	Average Ratio $\frac{O.P.}{G.P.}$	Maximum Deviation.	Mean Deviation.	Time Period.
0.1	144	Mar. 7	I	550.000	15	501.33	2.592	2.390	.202	1.085	.003	.002	26
0.1	163	Mar. 28	M	370,000	15	501.33	2 583	2.390	.193	1.081	.006	.005	52
0.2	149	Mar. 12	Q	180,000	15	501.33	5.071	4 780	.291	1.061	.005	.002	97
0.3	152	Mar. 15	T	535,000	9	454.14	7.615	7.170	.445	1.062	.004	.003	47
0.4	156	Mar. 19	G	110.000	9	454.14	10.130	9.560	.670	1.060	.003	.001	51
0.4	161	Mar. 23	I	285,000	9	454.14	10.117	9.560	.557	1.058	.008	.003	46
0.5	81	Jan. 20	G	367,000	15	501.33	12.737	11.950	.787	1.066	.002	.001	42
0.5	160	Mar. 21	R	162,000	15	501.33	12.750	11 950	.800	1 067	.002	.001	44
0.6	39	Nov. 19	O	350.000	5	637.60	15 370	14.339	1 031	1.072	.002	.001	36
0.6	34	Nov. 1	Z	550,000	6	412.00	15.390	14 339	1.051	1 073	.004	.002	28
0.7	49	Dec. 2	D	380,000	5	637.60	18.121	16 729	1.392	1.083	.004	.002	73
0.7	40	Dec. 2	U	380 000	6	412.00	18 115	16.729	1 386	1.083	.007	.003	65
0.8	48	Nov. 26	Z	570.000	5	637.60	20.915	19 119	1 796	1.093	.003	.001	37
0.8	44	Nov. 22	D	220.000	5	637.60	20.810	19.119	1.697	1.088	.004	.002	65
0.9	155	Mar. 17	D	550,000	15	501.33	23.721	21.509	2.212	1.103	.002	.001	93

TABLE B.

Concentration.	No. of Experiment.	Date.	Cell.	Resistance.	Monometer.	Volume.	Average O. P.	Theoretical Gas Pressure.	Difference.	Average Ratio $\frac{O.\ P.}{G.\ P.}$	Maximum Deviation.	Mean Deviation.	Time Period.
0.1	128	Mar. 7	H	370,000	21	533.85	2.527	2.390	.137	1.057	.002	.001	89
0.5	29	Nov. 6	N	180,000	15	501.33	12.393	11.950	.443	1.037	.002	.001	24
0.5	27	Nov. 6	O	366,000	6	412.00	12.612	11.950	.662	1.056	.002	.001	35
0.5	102	Feb. 8	Y	373,000	21	533.85	12 618	11.950	.668	1 056	.003	.001	164
0.6	36	Nov. 16	Y	386,000	15	501 33	15.262	14.339	.923	1.064	.006	.003	48
0.8	45	Nov. 22	L	260,000	15	501.33	20 667	19.119	1.548	1.081	.004	.002	70
0.9	62	Dec. 13	D	224.000	5	637 60	23.410	21.509	1.901	1.089	.003	.002	25
0.9	70	Dec. 21	Y	275,000	15	501.33	23.415	21.509	1.906	1.089	.002	.001	34
1.0	121	Mar. 3	P	370,000	21	533.85	26 285	23.899	2.384	1.100	.004	.002	65

TABLE C.

Concentration.	No. of Experiment.	Cell.	Monometer.	Ratio with First Volume.	Ratio with Second Volume.	Maximum Deviation.	Mean Deviation.	Time.
0.1	139	L	13	1.050	1.084	.005	.003	72
0.2	148	R	20	1.055	.....	.001	.001	24
0.3	151	I	20	1.055	.....	.002	.001	47
0.4	91	Y	13	1.042	1.068	.003	.001	45
0.4	93	X	13	1.046	1.071	.001	.001	25
0.5	85	P	11	1.049	.....	.001	.001	49
0 5	86	O	13	1.045	1.071	.001	.001	49
0.8	105	Z	24	1.080	1.101	.002	.001	78
0.9	71	H	22	1.072	.....	.002	.001	27
0.9	154	F	24	1.096	1.115	.002	.001	72
1.0	118	A_5(63)	24	1.106	1.124	.003	.001	51

THE MEASUREMENTS AND THEIR DISCUSSION.

Table A is a summary of the measurements which give ratios agreeing with those obtained recently at 0°, 5°, and 10°.[1]

In table B are to be found ratios lying between those obtained in the earlier work and those of table A.

In table C are some determinations which fulfill all the requirements of good measurements, except that a curious discrepancy in the volumes of the manometers occur, which at present cannot be explained.

The columns in the tables are, in order, the concentration of the solution in terms of *weight* normal, the number of the experiment, the date[2] when the experiment was started, the cell used, the resistance of the membrance in ohms at the close of the electrolytic renewal, the number of the manometer, its volume in calibration units at standard conditions of temperature and pressure, the average observed osmotic pressure in atmospheres, the theoretical gas pressure in atmospheres, the average difference between the observed osmotic pressure and the theoretical gas pressure, the average ratio of osmotic to gas pres-

1 Dissertations of Zies & Gill, 1909, and unpublished work at 10° done in 1909.

2 In the academic year 1909-1910.

sure, the maximum deviation in the ratio from the mean of all the observations, the mean deviation of the same, the time period in hours during which the ratio remained constant.

In tables A and B only those measurements are included which were made with manometers whose volumes at standard conditions of temperature and pressure were determined by the side tube method described in The American Chemical Journal for October, 1908. It will be seen that the manometers in table C are an entirely different set. The volumes of these latter were determined by comparison with a standard manometer. It was hoped, that, by the use of this standard manometer, the normal volumes of the experimental manometers could be calculated by employing a greater range of pressure. Accordingly, several manometers were compared with the standard. In the case of manometer 21 the volume as calculated by comparison with the standard under low pressures agreed very well with the volume as calculated by the side tube method. At pressures of from three to seven atmospheres however, a minimum in the calculated volumes were observed in all manometers compared with the standard, and at higher pressures the calculated volume steadily increased with increasing pressure.

This increase is probably due to the error in meniscus correction previously mentioned; but, since neither this, nor possible causes of the minimum, have as yet been studied quantitatively, the proper corrections cannot be applied. Obviously, the only course to pursue at present is to bring all the manometers to a comparable basis by determining their normal volumes by one method, preferably the side tube method, which is an absolute one. Unfortunately, a considerable number of measurements were made with manometers 11, 13, 20, 22 and 24 before there was an opportunity to determine their normal volumes by the side tube method. When 13 and 24 were so redetermined, their volumes were *apparently* altered. It is impossible to say at present to what the discrepancy is due, and consequently the ratios of table C cannot be placed with either those of table A or B. A discussion of which values should be taken in these measurements would be unprofitable in view of the total uncertainty attached to the manometer data. Furthermore, in certain cases the results are vitiated by the probability that the wrong volume of the manometer was chosen as the basis for the calculation of the initial "mechanical" pressure, and consequently, a concentration of the solution may have occurred, as previously shown to be possible, with a subsequent compensating dilution, and the saccharimeter would have indicated no change in concentration.

It is to be noted that the high ratios agree very well with those found at 0°, 5°, and 10° as the following table will show:

Weight Normal Concentration.

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0 9	1.0
0°	.....	1.061	1.059	1.061	1,069	1.076	1.084	1.094	1.104	1.115
5°	1.082	1.063	1.059	1.061	1.067	1.074	1.084	1.093	1.101	1.115
10°	1.083	1.061	.....	1.061	1.066	1.072	1.083	1.092	1.102	1.114
20°	1.083	1.061	1.062	1.059	1.067	1.073	1.083	1.091	1.103	. ...
mean	1.082	1.062	1.060	1.061	1.067	1.074	1.084	1.093	1.103	1.115

The ratios in table B, on the other hand, when compared with the old values found at 20°,[1] and with the mean values of the old series V to VIII,[2] are found to be above these older values in each case, and to lie between the lower ratios of the older series and the higher ratios of the more recent investigations. If it is permissible to omit experiment 29 simply because the 1.037 ratio is not in agreement with that of two other measurements of the same concentration, the relations of the ratios in table B to the mean of the ratios of series V to VIII and to the mean of the higher ratios given in the above table are clearly shown in the plotted curves.

LOW RATIOS OF FORMER WORK COMPARED WITH LOW RATIOS FOUND AT 20° THIS YEAR.

Weight Normal Concentration.

Series.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
VIII 20° mean of series.	1.055	1.051	1.038	1.042	1.045	1.060	1.066	1.077	1.084	1.093
V-VIII 10°-25°	1.054	1 047	1.039	1.040	1.045	1.056	1.060	1.070	1.081	1.068
Mean ratios in table B.	1.057	.....	.....	.....	1.050-56	1.064	.....	1.081	1.089	1.100

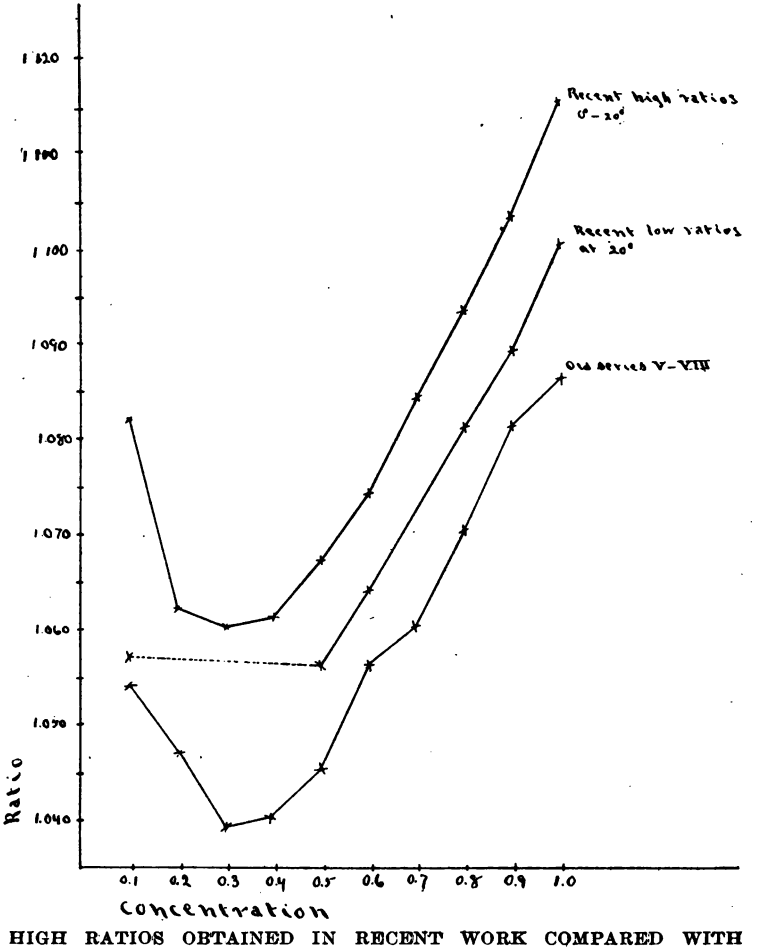
Perhaps the low values of table B are too few to say definitely that they constitute a series in themselves, but the proportionality between them is striking.

The sharp division between the ratios of table A and those of table B calls for discussion. The search for possible explanations will be found to be met with difficulties which are insuperable in the present state of our knowledge, but a discussion may be of profit.

At first thought it might be suspected that the discrepancies were due to the use of different manometers. Manometer 21 occurs only in table B and 9 only in table A. 9 is not suspected; and 21 is under only slight suspicion because a recent recalibration indicates a slight change in its bore, due perhaps to molecular changes in the glass. The curve of the recalibration has been used in the calculations.

Examining the dates of the measurements with 5, 6, and 15, the manometers which occur in both tables, we find that the

one low value with 5 occurred after four high values were obtained with it, while four low values with 15 were obtained before the six high values. On the other hand, the one low



HIGH RATIOS OBTAINED IN RECENT WORK COMPARED WITH HIGH RATIOS AT 20°.

value obtained with manometer 6 has its date sandwiched between those of the two high values. If, in subsequent work, it should be proved that the manometers need more frequent

1 Morse & Holland, Am. Chem. Jour., 41, 4 (1909).
2 ibid, page 275.

standardization than has been considered necessary, considerations such as the above may be of value.

Turning now to the cells, it is seen that D and O alone occur in both tables. It would be unfair, however, to attribute great significance to this, for an examination of a considerable number of measurements, which were rejected only because of a slight gain or loss in rotation, shows that other cells included in table A have given low ratios in spite of gains in the rotation of the solutions.

We might find in the conditions or known errors of the experiments some constant factor which will explain this sharp division in the ratios. Let us inquire if any such factor can be discovered.

It has been suggested that the low pressures might be due to an accumulation of copper salts in the cell wall during the electrolytic renewal of the membrane. Although it is difficult to see how this should affect certain measurements always to about the same degree, and not other measurements conducted under *apparently* the same conditions, the suggestion was taken as the basis of some experimental work. A cell, after subjection to the customary electrolytic process for the renewal of the membrane, was soaked for ten days in frequent changes of water. The total water was then evaporated, the residue of accumulated thymol ignited and evaporated with sulfuric acid. The residue of 6 mg. was considered as that of $CuSO_4$ soaked from the cell wall. Had this diffused from the cell wall, and, by very slow diffusion contaminated only that portion of the solution adjacent to the cell wall, it might have had a slight effect upon the observed osmotic pressure. It is impossible, however, to say what its distribution would have been. In some cases salts may diffuse out more rapidly than in others, while it is perhaps also possible, that the membrane, which inadvertently accumulates on the cell's exterior, may serve in some cases to retain inclosed salts quite completely.

Another cell, after the customary rinsing, was soaked for two hours after electrolysis, the time usually allowed between electrolysis and the setting up of a cell for a measurement. The residue obtained in this case was considerably below that which can be estimated by ordinary gravimetric means.

A curious fact, with which this idea that the cell wall accumulates salt has been connected is observed when a cell is used more or less continuously without giving it the "rest" and the soaking out, which has become a regular part of the procedure. When not given a sufficient "rest" with soaking, cells have developed constant but low pressures. A notable case of this was observed some two years ago, and a possible explanation is,

that in rushing the cells into frequent measurements the repeated electrolytic renewal of the membrane plugged the cell wall with salts, for the soaking out of which sufficient time was not allowed. In the present investigation each cell has been soaked about a week between measurements made with it.

Another attempt was made to gain an experimental basis for the supposed influence of salts accumulating in, and diffusing out, from the cell wall. It has been found best to renew the membranes in 0.1n $CuSO_4$, but the concentration of $CuSO_4$ used as membrane former in a measurement is 0.01n. It would seem, however, that if the membranes were renewed in a solution of the same low concentration as that into which they are placed during a measurement, there would be less chance of carrying over to this dilute solution, copper sulfate which might have accumulated while the cell was in the more concentrated solution ordinarily used. This was tried, but the uncertainty with any cell is so great that no conclusions can be drawn.

Because of the difficulty of drawing conclusions from the data obtained in any of these methods of attack, the question was investigated directly by setting up cells with very dilute solutions and open manometers capable of showing very slight differences in pressure, the plan being to see whether any difference of pressure could be observed between cases when every chance was given for the cells to lose the accumulated salt, and cases when the cells were supposed to have had an opportunity to accumulate salts within their walls. The experiments though, at first sight, both confirming and contradicting the hypothesis they were designed to test, were found to be so involved by reason of some unexpected phenomena that the evidence desired can only be untangled after further investigations.

It is, of course, possible that a minute leak in the membrane could just counterbalance the tendency of the solution to develop a maximum pressure. It would seem, however, that leaks, even if they allowed constant pressures to be observed, would cause greater divergence in the results obtained in different instances. Attention is called to the agreement between experiments 27 and 102 and between experiments 62 and 70. Furthermore the fact that a very careful study of the original and final solutions with the saccharimeter in experiments 128 and 102 showed no change in concentration after the period of 89 hours in one case, and 164[1] hours in the other, argues against leakage.

1 The maintenance of constant pressures for periods of this length would seem to indicate a truly semipermeable membrane.

A calculation will perhaps bring this point out more clearly. If the solution should leak through the membrane and not be replaced by water, we would observe a steady drop of the mercury in the manometer. In the case of two 0.9n measurements, both made with manometer 15, no such steady drop was observed, and the actual difference between the observed volume which indicated the low ratio and that which indicated the high ratio was only 0.3 calibration unit, or about 0.06 cubic millimeter. It is, therefore, necessary to assume that the observed pressure was kept constant by the intake of sufficient water to replace the volume of solution which had leaked out. Dilution of the solution must therefore have occurred. Now, let us say that 10 milligrams of sugar escaped, and the solution containing this was replaced by an equal volume of water. The capacity of the cell is about 20 c.c. and, had twenty c.c. of the 0.9n solution been diluted by the loss of 10 milligrams of sugar, its rotation would have been diminished by almost 0.2, an easily detected loss. But let us assume that even this escaped detection, and, furthermore, that while the cell was quiet, the dilution only occurred in the fourth of the total 20 c.c. which lay nearest the membrane. This 5 c.c. would then have had its sugar content reduced from the original 1.5273 g. to 1.5173 g.[1] The observed osmotic pressure of the first concentration is 23.721 atmospheres, and of the second would be about 23.566 atmospheres, a difference of 0.155 atmosphere. The actual difference in pressure between experiments 155 and 70 was 0.306 atmosphere, or about twice the amount which could be accounted for when every advantage is given to the above argument. In this calculation an assumption has been made which is perhaps false to the actual phenomenon. It was assumed that the observed low pressure was a function of the dilution of the solution. A pseudo equilibrium might have obtained, the solution leaking out with extreme slowness, and the water entering at the same slow compensating rate. The dilution in this case might have been inappreciable at the end of even a considerable period. The data of the intake of water through the membranes are insufficient to base any calculations upon, and therefore it can only be said that a remarkably exact and constant adjustment of intake to leak must have occurred in each case to produce a pseudo equilibrium of the constant magnitude observed.

Again, if the original solutions were wrongly made up, the error would be detected in the rotation.

Let us now consider another point. In calling attention to

1 The error in assuming the weight concentration to be a volume concentration is negligible in this calculation.

the necessity of very accurate temperature regulation, Morse and Holland stated in their article, *The Regulation of Temperature in the Measurement of Osmotic Pressure,*[1] that "the ideal would be a regulation so exact that not even the form of the mercury meniscus in the manometer could be sensibly affected by variations in the volume of the inclosed solution," and ".... even the variation in the form of the meniscus becomes a matter of importance whenever it is attempted to measure the osmotic pressure of concentrated solutions." If, for example, with manometer 15 and the pressure of a 0.9n solution, the observed volume plus the double meniscus correction is 22.57, and, owing to slight variations in temperature, the mercury has risen and then fallen leaving the meniscus flat, then one half the double meniscus correction has been added erroneously. One-half the double meniscus correction for manometer 15 is 0.08 calibration unit. Subtracting this from the 22.57 we get for the true volume of the nitrogen 22.49 calibration units. In the particular observation taken as the basis for this calculation the 22.57 volume was found to give a ratio of 1.090. Had 22.49 been the true volume it would have given in the calculation a ratio of 1.094, while the maximum obtained for a 0.9n solution is 1.103. Obviously, errors in meniscus correction produce the greatest effect in the calculated pressures of high concentrations, and, since the discrepancy which might be attributed to a complete flattening of the meniscus effects the ratio for a 0.9n solution but four points in the third decimal place, as shown, it would have proportionally less influence upon the ratios for lower concentrations. Further, more than a slight flattening of the meniscus would not have escaped notice in the reading. Therefore it is to be concluded that this source of error, when taken *alone*, is insufficient to explain the differences between the ratios of table A and those of table B, although it is of considerable import, as the 0.004 point possible error in the 0.9n ratio will show.

It is, of course, possible that a "heaping" of all these errors in one direction could cause a low pressure to be observed in one case, while the maximum was allowed to develop in another case. This is highly improbable in view of the fact that only one distinctly anomalous value has been observed. There is, therefore, every evidence that some constant difference in the conditions, as yet not fully known, has caused the discrepancy. Certain possible sources have long been recognized; but it has been the policy in the researches in this laboratory to attack those problems which seemed of greater moment, and to leave

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1 Am. Chem. Jour., Feb., 1909.

other smaller sources of error till the larger ones have been removed. At present our time and thought is concentrated upon the manometers, and manometers of a type which will, for the most part, eliminate the errors of meniscus correction are under construction. With the development of these and other improvements in the apparatus the time is approaching when the accuracy of the measurements will exceed even that which now obtains, and the absolute, rather than the relative, osmotic pressures, may be the subject of future investigations. It may therefore be well to call attention to certain conditions which far more important matters have forced into the background to await more thorough investigation, but which are of live interest, not only because they are recognized as having a possible influence upon the true osmotic pressure, but because they may possibly have had something to do with the discrepancies observed in the present investigation. Because of the scantiness of quantitative evidence for or against these considerations, they will be discussed under the heading—

THEORETICAL CONSIDERATIONS.

The membrane formers, that is the potassium ferrocyanid, which is put into the sugar solution and the copper sulfate into which the cell is placed during a measurement, were calculated to be isosmotic from considerations of their freezing point lowerings and conductivities.[1] The concentration of osmotically active particles in solutions of each of these salts at the dilution used is still in doubt, but we have some evidence that the solutions in use as membrane formers are not isosmotic.[2] In addition it is known, that there is a considerable difference of potential, when a potassium ferrocyanid solution of the concentration used is placed in the cell, and the cell dipped into a copper sulfate solution of the concentration used in a measurement. When measured with platinum electrodes, by a potentiometer, and at constant temperature, the two solutions separated by the membrane of cell Z, shortly after Z was taken down from a measurement, showed a difference of potential of 0.452 volts, declining to 0.449 volts in five minutes. With cell P, two hours after it had been subjected to the electrolytic process for the renewal of the membrane, the difference of potential was 0.752 volts, which declined steadily to 0.519 volts at the end of three hours. In each case the electrode in the copper solution was positive to that in the ferrocyanid solution, as might be expected if part at least of the difference in

1 Am. Chem. Jour., 34, 31; 34, 311.
2 Attention was called to the significance of this on page

potential is due to the establishment of a liquid element. The curious behavior of a cell's electrical resistance during the round of its treatment is also to be noted. When treated electrolytically for the renewal of the membrane, the resistance gradually rises in the course of an hour to its customary maximum, which for some cells is as high as 500,000 ohms, and has been known to reach 1,000,000 ohms. When removed from the electrolizing bath, and allowed to soak, the cell is found to show a declining resistance, which, in the course of a few hours, may become one-fifth its former value; and, if the resistance is taken immediately after the cell has been taken down from a measurement, it is found to vary considerably in different cases, and in certain instances to be close to the initial resistance, and in other cases to have declined greatly.

From the above considerations it may be inferred that we may possibly have to deal, not only with a difference in the osmotic concentrations of the two membrane formers, but also with the possibility that adjustments towards electrolytic equilibrium may take place in *varying* degrees. It is to be hoped that further study of this problem may throw some light on the discrepancies observed in the present investigation.

A further theoretical consideration is now presented, not because any great importance is to be attached to a certain parallelism between the theory and certain facts which have become prominent in the work, but because it is hoped that the idea may be of interest.

It has been observed, that to produce a membrane capable of allowing the development of a maximum osmotic pressure, there are required weeks and often months, during which the copper ferrocyanid membrane is repeatedly packed by the electrolytic process using as high a potential[1] as is consistent with the safety of the membrane. Weak spots in the membrane are then burst by subjecting them to high osmotic pressure, with the membrane formers present, and the rents are mended by electrolysis. Furthermore, it has been found necessary to renew the membrane between each measurement. Membranes which have not been so repacked just previous to a measurement have been found not to allow the development of the highest attained pressures, but permit a steady decline in pressure. At times a new cell will give a constant pressure below the maximum, but never, until after continued treatment, a maximum. There is also some evidence, obtained this year by Dr. Holland and Mr. Meyers, and confirmed by past experience, that the efficiency of a membrane is improved when it

1. 110 volts has been found best.

is packed at a higher temperature than that at which the measurement with it is made, the supposition being that the coefficients of expansion of membrane and cell wall are such, that, when the temperature is lowered, the membrane is packed closer. There is, therefore, some basis for believing that the development of a maximum osmotic pressure is intimately connected with a close texture of the membrane.

Let us now assume that the membrane is semipermeable by reason of a net-work of exceedingly fine capillaries. Moore[1] on the basis of this assumption, deduces the following relation connecting the surface tension of solutions with their osmotic pressure:

$$(1.) \qquad 2\,\Pi\, r\, T = \Pi\, r^2\, P$$

$$\text{whence } P = \frac{2T}{r}$$

"Where T is the difference between the surface tension of the solution and that of the pure solvent, P the osmotic pressure[2] in this solution, supposed to be due to the action of this difference in surface-tension, and r the radius of a capillary opening, placing the solution and the solvent in communication."

According to the equation, $P = \frac{2T}{r}$, P is a function of r and must increase as r diminishes; that is, as the membrane is packed closer and closer and the capillaries become smaller and smaller. Moore then deduces that when the radius of the capillaries become so small that the surface tension acts not only at the perimeter but over the whole cross section of a capillary, a condition which will be realized when the diameter of the capillary approaches the diameter of molecules, then equation (1) becomes:

$$\Pi\, r^2\, t = \Pi\, r^2\, P$$

$$\text{or } t = P$$

where t is the difference for maximum value of molecuar attraction for solution and solvent. Therefore, with capillaries of molecular dimensions, the osmotic pressure would cease to be a function of r and a maximum would obtain.

It may be well to call attention to the fact that equation (1) is the condition of a pseudo equilibrium. According to well-known thermodynamical reasoning P, "the osmotic pressure" as a function of r could in no sense of the word be taken as

1 Phil. Mag., 38, 279 (1894), Fifth Series.

2 Referring to Moore's article, it will be seen that less danger of confusion would have been incurred had P been termed the hydrostatic pressure.

the true osmotic pressure of a solution in equilibrium with the solvent.

Attention is called to the deduction simply to show the interesting parallelism between what it suggests to the mind, and the inference which is aroused by a consideration of the methods found necessary in this laboratory to produce perfect membranes.

In conclusion it may be said, that no one of the considerations, experimental or theoretical, which have been advanced in this paper can be claimed in the present state of our knowledge to be adequate for the explanation of the discrepancy between the two sets of ratios; and, with one exception, that the constancy of the discrepancy is such as to seem to preclude the argument that errors were "heaped." Yet all considerations alike seem to militate against the low and in defense of the high values. The high ratios are therefore provisionally *judged* to be the more reliable.

SUMMARY.

A large supply of cane sugar of known high purity has been prepared, in order that the measurements in progress during the past year, as well as those to be made for some time to come, may have the advantage that they were conducted with a single stock of sugar of guaranteed purity.

Minor improvements have been made in the apparatus used at 20°.

The measurements made of the osmotic pressures of cane sugar solutions at 20° have furnished, on the one hand, data which confirm the conclusion deduced from measurements at other temperatures, namely, that the temperature coefficient of the osmotic pressure of cane sugar solutions ranging in concentration from one tenth *weight* normal to normal follows closely the temperature coefficient of gases within the range of temperature 0°-20°.

And, on the other hand, there have accumulated in this investigation a few data which, if taken without due consideration, might be claimed to stand at slight variance with the former conclusion. But these, it is believed, are of more scientific value when used in calling attention to certain conditions and certain problems, which, it is hoped, further investigation will clarify to the advantage of whatever conclusions the evidence yet to be accumulated may point.

BIOGRAPHICAL.

The author was born at Tivoli-on-the-Hudson, New York, August 17th, 1884. He prepared for college at the Hotchkiss School, Lakeville, Connecticut. He received his A. B. at Williams College with the class of 1907, and the year after graduation was Assistant in Chemistry. The degree of Master of Arts was conferred upon him in 1908 by Williams College for studies in Chemistry and Physics, and the following year he entered upon his work for the degree of Doctor of Philosophy at the Johns Hopkins University, with Chemistry as major subject and Physical Chemistry and Physics as subordinate studies. He has held a University Fellowship during the academic year 1909-1910.